

#### IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Atsutaka MANABE et al.

Examiner: Shean Chiu WU

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Title: LIQUID-CRYSTAL MEDIUM CONTAINING MONOFLUOROTERPHENYL

**COMPOUNDS** 

### SUBMISSION OF VERIFIED TRANSLATION OF PRIORITY DOCUMENT

Commissioner for Patents P.O. Box 1450 Alexandria, VA 22313-1450

Sir:

Applicants attach herewith a verified translation of the German Priority Document No. 103 31 490.3, filed July 11, 2003.

The Commissioner is hereby authorized to charge any fees associated with this response or

credit any overpayment to Deposit Account No. 13-3402.

Respectfully submitted,

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## IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In the matter of an application for a German Patent

with the file reference 103 31 490.3 filed on 11 July 2003 in the name of Merck Patent GmbH, Darmstadt, Germany,

and in the matter of an application for a United States Patent.

I, Dr. Ashwood Stephen DRANE, B.Sc., Ph.D., BDÜ, translator to SD Translations Ltd. of Beechwood, Chivery, Tring, Hertfordshire, HP23 6LD, England, do solemnly and sincerely declare:

- 1. That I am a citizen of the United Kingdom of Great Britain and Northern Ireland.
- 2. That I am well acquainted with the German and English languages and am a competent translator thereof.
- 3. That the following is to the best of my knowledge and belief a true and correct translation of the above-referenced patent application and the Official Certificate attached thereto

Dated this 5th day of February 2008

Dr. Ashwood Stephen Drane

### FEDERAL REPUBLIC OF GERMANY



# Priority certificate regarding the filing of a patent application

File reference:

103 31 490.3

Date of filing:

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Merck Patent GmbH,

64293 Darmstadt/DE

Title:

Liquid-crystalline medium

IPC:

C 09 K, C 07 C, G 09 F

The attached pages are a correct and accurate reproduction of the original documents of this patent application.

Seal

Munich, 22 April 2004

German Patent and Trademark Office

On behalf of

The President

[signature]

**Faust** 

Merck Patent Gesellschaft mit beschränkter Haftung 64271 Darmstadt

### Liquid-crystalline medium

#### Liquid-crystalline medium

The present invention relates to a liquid-crystalline medium, to the use thereof for electro-optical purposes, and to electro-optical display devices which contain this medium.

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Liquid crystals are used principally as dielectrics in display devices, since the optical properties of such substances can be modified by an applied voltage. Electro-optical devices based on liquid crystals are extremely well known to the person skilled in the art and can be based on various effects. Examples of such devices are cells having dynamic scattering, DAP (deformation of aligned phases) cells, guest/host cells, TN cells having a twisted nematic structure, STN (supertwisted nematic) cells, SBE (super-birefringence effect) cells and OMI (optical mode interference) cells. The commonest display devices are based on the Schadt-Helfrich effect and have a twisted nematic structure.

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The liquid-crystal materials must have good chemical and thermal stability and good stability to electric fields and electromagnetic radiation. Furthermore, the liquid-crystal materials should have low viscosity and produce short addressing times, low threshold voltages and high contrast in the cells.

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They should furthermore have a suitable mesophase, for example a nematic or cholesteric mesophase for the above-mentioned cells, at the usual operating temperatures, i.e. in the broadest possible range above and below room temperature. Since liquid crystals are generally used as mixtures of a plurality of components, it is important that the components are readily miscible with one another. Further properties, such as the electrical conductivity, the dielectric anisotropy and the optical anisotropy, have to satisfy various requirements depending on the cell type and area of application. For example, materials for cells having a twisted nematic structure should have positive dielectric anisotropy and low electrical conductivity.

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For example, for matrix liquid-crystal displays with integrated non-linear elements for switching individual pixels (MLC displays), media having large positive dielectric anisotropy, broad nematic phases, relatively low birefringence, very high specific resistance, good UV and temperature stability and low vapour pressure are desired.

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Matrix liquid-crystal displays of this type are known. Non-linear elements which can be used for individual switching of the individual pixels are, for example, active elements (i.e. transistors). The term "active matrix" is then used, where a distinction is made between two types:

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- MOS (metal oxide semiconductor) or other diodes on a silicon wafer as substrate.
- 2. Thin-film transistors (TFTs) on a glass plate as substrate.

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The use of single-crystal silicon as substrate material restricts the display size, since even modular assembly of various part-displays results in problems at the joints.

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In the case of the more promising type 2, which is preferred, the electrooptical effect used is usually the TN effect. A distinction is made between two technologies: TFTs comprising compound semiconductors, such as, for example, CdSe, or TFTs based on polycrystalline or amorphous silicon. Intensive work is being carried out worldwide on the latter technology.

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The TFT matrix is applied to the inside of one glass plate of the display, while the other glass plate carries the transparent counterelectrode on its inside. Compared with the size of the pixel electrode, the TFT is very small and has virtually no adverse effect on the image. This technology can also be extended to fully colour-capable displays, in which a mosaic of red, green and blue filters is arranged in such a way that a filter element is opposite each switchable pixel.

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The TFT displays usually operate as TN cells with crossed polarisers in transmission and are back-lit.

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The term MLC displays here covers any matrix display with integrated non-linear elements, i.e., besides the active matrix, also displays with passive elements, such as varistors or diodes (MIM = metal-insulator-metal).

MLC displays of this type are particularly suitable for TV applications (for

example pocket TVs) and for high-information displays for computer applications (for example laptops) and in automobile and aircraft construction. Besides problems regarding the angle dependence of the contrast and the response times, difficulties also arise in MLC displays due to insufficiently high specific resistance of the liquid-crystal mixtures [TOGASHI, S., SEKI-GUCHI, K., TANABE, H., YAMAMOTO, E., SORIMACHI, K., TAJIMA, E., WATANABE, H., SHIMIZU, H., Proc. Eurodisplay 84, Sept. 1984:

A 210-288 Matrix LCD Controlled by Double Stage Diode Rings, p. 141 ff, Paris; STROMER, M., Proc. Eurodisplay 84, Sept. 1984: Design of Thin Film Transistors for Matrix Addressing of Television Liquid Crystal Dis-

plays, p. 145 ff, Paris]. With decreasing resistance, the contrast of an MLC display deteriorates, and the problem of after-image elimination may occur. Since the specific resistance of the liquid-crystal mixture generally drops over the life of an MLC display owing to interaction with the interior surfaces of the display, a high (initial) resistance is very important in order to

achieve acceptable service lives. In particular in the case of low-volt mixtures, it was hitherto impossible to achieve very high specific resistance values. It is furthermore important that the specific resistance exhibits the smallest possible increase with increasing temperature and after heating and/or UV exposure. The low-temperature properties of the mixtures from

the prior art are also particularly disadvantageous. It is demanded that no crystallisation and/or smectic phases occur, even at low temperatures, and the temperature dependence of the viscosity is as low as possible. The known MLC displays do not meet these requirements.

There thus continues to be a great demand for MLC displays having very high specific resistance at the same time as a large working-temperature range, short response times even at low temperatures and low threshold voltage which do not have the said disadvantages, or only do so to a reduced extent.

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In addition to liquid-crystal displays which use backlighting, i.e. are operated transmissively and if desired transflectively, reflective liquid-crystal displays are also particularly interesting. These reflective liquid-crystal displays use the ambient light for information display. They thus consume significantly less energy than back-lit liquid-crystal displays having a corresponding size and resolution. Since the TN effect is characterised by very good contrast, reflective displays of this type can even be read well in bright ambient conditions. This is already known of simple reflective TN displays, as used, for example, in watches and pocket calculators. However, the principle can also be applied to high-quality, higher-resolution active matrix-addressed displays, such as, for example, TFT displays. Here, as already in the transmissive TFT-TN displays which are generally conventional, the use of liquid crystals of low birefringence ( $\Delta n$ ) is necessary in order to achieve low optical retardation (d  $\cdot$   $\Delta$ n). This low optical retardation results in usually acceptable low viewing-angle dependence of the contrast (cf. German Patent 30 22 818). In reflective displays, the use of liquid crystals of low birefringence is even more important than in transmissive displays since the effective layer thickness through which the light passes is approximately twice as large in reflective displays as in transmissive displays having the same layer thickness.

The advantages of reflective displays over transmissive displays, besides the lower power consumption (since backlighting is unnecessary), are the space saving, which results in a very small physical depth, and the reduction in problems due to temperature gradients caused by different degrees of heating by the backlighting.

In TN (Schadt-Helfrich) cells, media are desired which facilitate the following advantages in the cells:

- extended nematic phase range (in particular at low temperatures),
- the ability to switch at extremely low temperatures (outdoor use, automobiles, avionics),

- elevated resistance against UV radiation (longer life),
- low rotational viscosities,
- low threshold (addressing) voltage and

 high birefringence for thinner layer thicknesses and thus shorter response times.

The media available from the prior art do not allow these advantages to be achieved while simultaneously retaining the other parameters.

In the case of supertwisted (STN) cells, media are desired which enable greater multiplexability and/or lower threshold voltages and/or broader nematic phase ranges (in particular at low temperatures). To this end, a further widening of the available parameter latitude (clearing point, smectic-nematic transition or melting point, viscosity, dielectric parameters, elastic parameters) is urgently desired.

In addition, the trend in monitor and TV applications is towards evershorter response times. The display manufacturers are reducing the response time through the use of displays of smaller layer thickness. At constant optical path length  $d \cdot \Delta n$ , this requires liquid-crystal mixtures of greater  $\Delta n$ . In addition, the use of liquid-crystal mixtures of low rotational viscosity likewise results in a shortening of the response times.

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The present invention thus had the object of providing media for MLC, TN or STN displays of this type, preferably for MLC and TN displays and particularly preferably for transmissive TN displays, which do not have the above-mentioned disadvantages or only do so to a reduced extent, and at the same time preferably have very low rotational viscosities  $\gamma_1$  and relatively high optical anisotropy values  $\Delta n$ . The mixtures according to the invention should preferably find use in transmissive applications.

It has now been found that these objects can be achieved if the media according to the invention are used in displays.

The present invention thus relates to a liquid-crystalline medium based on a mixture of polar compounds of positive or negative dielectric anisotropy which is characterised in that it comprises one or more compounds of the general formula I

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$$R^1$$
  $O$   $O$   $R^2$ 

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in which

R<sup>1</sup> and R<sup>2</sup>

denote H, an alkyl radical having 1 to 12 C atoms which is

unsubstituted, monosubstituted by CN or CF<sub>3</sub> or at least monosubstituted by halogen, where, in addition, one or more CH<sub>2</sub> groups in these radicals may each, independently of

each, independently of one another, identically or differently,

one another, be replaced by -O-, -S-, -CH=CH-,

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-C≡C-, -CO-, -CO-O-, -O-CO- or -O-CO-O- in such a way that O atoms are not linked directly to one another.

The compounds of the formula I have a broad range of applications. These compounds can either serve as base materials of which liquid-crystalline media are predominantly composed, or they can be added to liquid-crystalline base materials from other classes of compound in order, for example, to modify the dielectric and/or optical anisotropy of a dielectric of this type and/or to optimise its threshold voltage and/or its viscosity.

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In the pure state, the compounds of the formula I are colourless and form liquid-crystalline mesophases in a temperature range which is favourably located for electro-optical use. They are stable chemically, thermally and to light.

If R<sup>1</sup> and/or R<sup>2</sup> denote an alkyl radical, this may be straight-chain or branched. It is preferably straight-chain, has 1, 2, 3, 4, 5, 6, 7, 8 or 9 C

atoms and accordingly preferably denotes methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl or nonyl, furthermore decyl, undecyl or dodecyl. Groups having 1 to 5 carbon atoms are particularly preferred.

If R<sup>1</sup> and/or R<sup>2</sup> denote an alkoxy radical, this may be straight-chain or branched. It is preferably straight-chain, has 1, 2, 3, 4, 5, 6, 7, 8 or 9 C atoms and accordingly preferably denotes methoxy, ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy, octoxy or nonoxy, furthermore decoxy or undecoxy.

If R¹ and/or R² denote an oxaalkyl radical, this may be straight-chain or branched. It is preferably straight-chain, has 1, 2, 3, 4, 5, 6, 7, 8 or 9 C atoms and accordingly preferably denotes 2-oxapropyl (= methoxymethyl), 2- (= ethoxymethyl) or 3-oxabutyl (= 2-methoxyethyl), 2-, 3- or 4-oxapentyl, 2-, 3-, 4- or 5-oxahexyl, 2-, 3-, 4-, 5- or 6-oxaheptyl, 2-, 3-, 4-, 5-, 6- or 7-oxaoctyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-oxanonyl or 2-, 3-, 4-, 5-, 6-, 7-, 8- or 9-oxadecyl.

If R<sup>1</sup> and/or R<sup>2</sup> denote an alkyl radical in which one CH<sub>2</sub> group has been replaced by -CH=CH-, this may be straight-chain or branched. It is preferably straight-chain and has 2 to 10 C atoms. Accordingly, it is particularly preferably vinyl, prop-1- or -2-enyl, but-1-, -2- or -3-enyl, pent-1-, -2-, -3- or -4-enyl, hex-1-, -2-, -3-, -4- or -5-enyl, hept-1-, -2-, -3-, -4-, -5- or -6-enyl, oct-1-, -2-, -3-, -4-, -5-, -6- or -7-enyl, non-1-, -2-, -3-, -4-, -5-, -6-, -7- or -8-enyl, or dec-1-, -2-, -3-, -4-, -5-, -6-, -7-, -8- or -9-enyl.

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If R<sup>1</sup> and/or R<sup>2</sup> denote an alkyl radical in which one CH<sub>2</sub> group has been replaced by -O- and one has been replaced by -CO-, these are preferably adjacent. These thus contain an acyloxy group -CO-O- or an oxycarbonyl group -O-CO-. These are preferably straight-chain and have 2 to 6 C atoms. Accordingly, they particularly preferably denote acetoxy, propionyloxy, butyryloxy, pentanoyloxy, hexanoyloxy, acetoxymethyl, propionyloxymethyl, butyryloxymethyl, pentanoyloxymethyl, 2-acetoxyethyl, 2-propionyloxyethyl, 2-butyryloxyethyl, 3-acetoxypropyl, 3-propionyloxypropyl, 4-acetoxybutyl, methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl, butoxycarbonyl, pentoxycarbonyl, methoxycarbonylmethyl, ethoxycarbonylmethyl,

propoxycarbonylmethyl, butoxycarbonylmethyl, 2-(methoxycarbonyl)ethyl, 2-(ethoxycarbonyl)ethyl, 2-(propoxycarbonyl)ethyl, 3-(methoxycarbonyl)-propyl, 3-(ethoxycarbonyl)propyl or 4-(methoxycarbonyl)butyl.

If R<sup>1</sup> and/or R<sup>2</sup> denote an alkyl radical in which one CH<sub>2</sub> group has been replaced by unsubstituted or substituted -CH=CH- and an adjacent CH<sub>2</sub> group has been replaced by CO, CO-O or O-CO, this may be straight-chain or branched. It is preferably straight-chain and has 4 to 12 C atoms. Accordingly, it is particularly preferably acryloyloxymethyl, 2-acryloyloxyethyl, 3-acryloyloxypropyl, 4-acryloyloxybutyl, 5-acryloyloxypentyl, 6-acryloyloxyhexyl, 7-acryloyloxyheptyl, 8-acryloyloxyoctyl, 9-acryloyloxynonyl, 10-acryloyloxydecyl, methacryloyloxymethyl, 2-methacryloyloxypentyl, 3-methacryloyloxypropyl, 4-methacryloyloxybutyl, 5-methacryloyloxypentyl, 6-methacryloyloxyhexyl, 7-methacryloyloxyheptyl, 8-methacryloyloxyoctyl or 9-methacryloyloxynonyl.

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If  $R^1$  and/or  $R^2$  denote an alkyl or alkenyl radical which is monosubstituted by CN or  $CF_3$ , this radical is preferably straight-chain. The substitution by CN or  $CF_3$  is possible in any desired position.

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If  $R^1$  and/or  $R^2$  denote an alkyl or alkenyl radical which is at least monosubstituted by halogen, this radical is preferably straight-chain and halogen preferably denotes F or Cl. In the case of polysubstitution, halogen preferably denotes F. The resultant radicals also include perfluorinated radicals. In the case of monosubstitution, the fluorine or chlorine substituent can be in any desired position, but preferably in the  $\omega$ -position.

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Compounds of the formula I which contain wing groups R<sup>1</sup> and/or R<sup>2</sup> which are suitable for polymerisation reactions are suitable for the preparation of liquid-crystalline polymers.

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Compounds of the formula I containing branched wing groups R<sup>1</sup> and/or R<sup>2</sup> may occasionally be of importance owing to better solubility in the conventional liquid-crystalline base materials, but in particular as chiral dopants if they are optically active. Smectic compounds of this type are suitable as components of ferroelectric materials.

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Compounds of the formula I having  $S_A$  phases are suitable, for example, for thermally addressed displays.

Branched groups of this type generally contain not more than one chain branch. Preferred branched radicals R<sup>1</sup> and/or R<sup>2</sup> are isopropyl, 2-butyl (= 1-methylpropyl), isobutyl (= 2-methylpropyl), 2-methylbutyl, isopentyl (= 3-methylbutyl), 2-methylpentyl, 3-methylpentyl, 2-ethylhexyl, 2-propylpentyl, isopropoxy, 2-methylpropoxy, 2-methylbutoxy, 3-methylpentoxy, 2-methylpentoxy, 3-methylpentoxy, and 1-methylheptoxy.

If R¹ and/or R² denote an alkyl radical in which two or more CH₂ groups have been replaced by -O- and/or -CO-O-, this may be straight-chain or branched. It is preferably branched and has 3 to 12 C atoms. Accordingly, it is particularly preferably biscarboxymethyl, 2,2-biscarboxyethyl, 3,3-biscarboxypropyl, 4,4-biscarboxybutyl, 5,5-biscarboxypentyl, 6,6-biscarboxyhexyl, 7,7-biscarboxyheptyl, 8,8-biscarboxyoctyl, 9,9-biscarboxynonyl, 10,10-biscarboxydecyl, bis(methoxycarbonyl)methyl, 2,2-bis(methoxycarbonyl)-butyl, 3,3-bis(methoxycarbonyl)propyl, 4,4-bis(methoxycarbonyl)-butyl, 5,5-bis(methoxycarbonyl)pentyl, 6,6-bis(methoxycarbonyl)hexyl, 7,7-bis(methoxycarbonyl)heptyl, 8,8-bis(methoxycarbonyl)octyl, bis(ethoxycarbonyl)methyl, 2,2-bis(ethoxycarbonyl)ethyl, 3,3-bis(ethoxycarbonyl)-propyl, 4,4-bis(ethoxycarbonyl)butyl or 5,5-bis(ethoxycarbonyl)pentyl.

R<sup>1</sup> and/or R<sup>2</sup> preferably, independently of one another, identically or differently, denote H, a straight-chain alkyl radical having 1 to 9 C atoms or a straight-chain alkenyl radical having 2 to 9 C atoms.

Preferred compounds of the formula I are consequently selected from the group of the compounds of the following sub-formulae Ia to Id, where subformula Ia is particularly preferred:

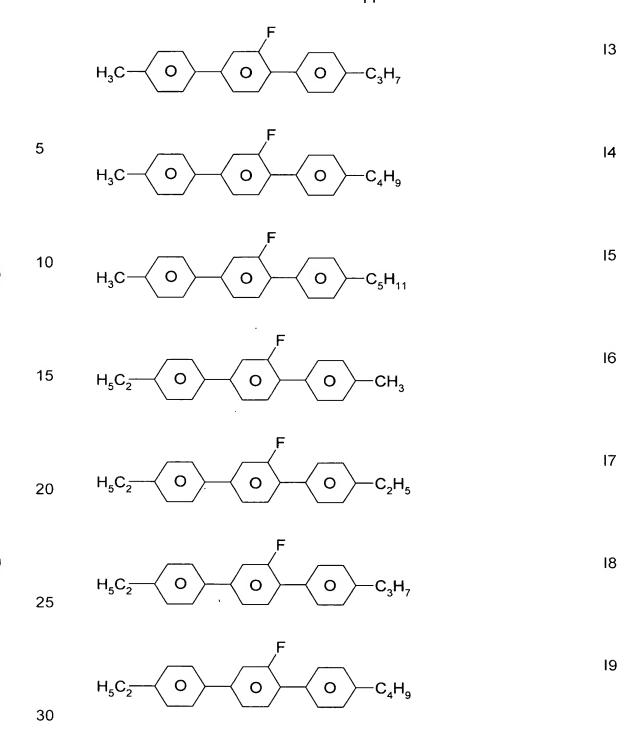
10 alkenyl<sup>1</sup> O O alkenyl<sup>2</sup>

where, in the formulae Ia to Id, the term "alkyl<sup>1</sup>" and "alkyl<sup>2</sup>" in each case, independently of one another, identically or differently, denotes a hydrogen atom or an alkyl radical having 1 to 9 C atoms, preferably a straight-chain alkyl radical having 1 to 5 C atoms, and the term "alkenyl<sup>1</sup>" and "alkenyl<sup>2</sup>" in each case, independently of one another, identically or differently, denotes an alkenyl radical having 2 to 9 C atoms, preferably a straight-chain alkenyl radical having 2 to 5 C atoms.

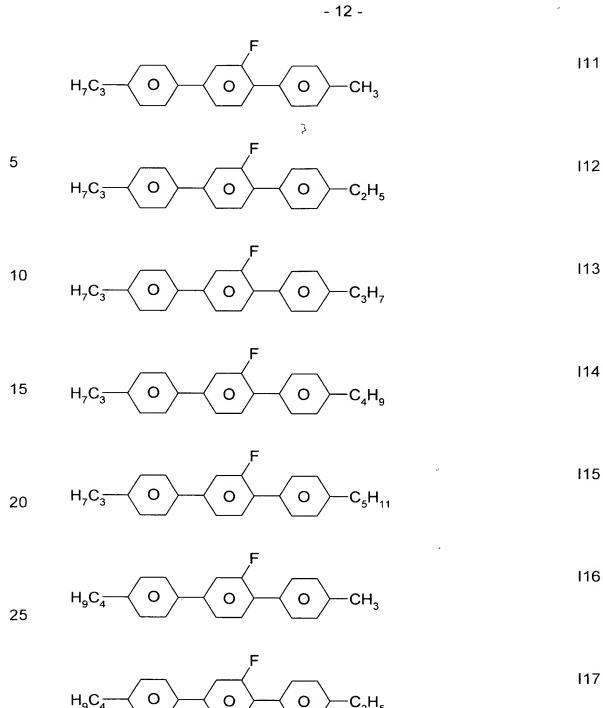
Preferred compounds of the formula I are consequently selected from the group of the compounds of the following sub-formulae I1 to I25:

$$H_3C$$
  $O$   $O$   $O$   $CH_3$ 

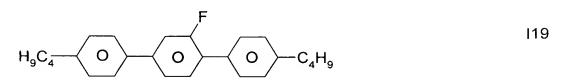
$$H_3C \longrightarrow O \longrightarrow O \longrightarrow C_2H_5$$



 $H_5C_2$  O O  $C_5H_{11}$ 



$$H_9C_4$$
 O O  $C_3H_7$ 



$$H_{11}C_{5} \longrightarrow O \longrightarrow CH_{3}$$

$$H_{11}C_{5} \longrightarrow O \longrightarrow O \longrightarrow C_{2}H_{5}$$

$$H_{11}C_{5} \longrightarrow O \longrightarrow O \longrightarrow C_{4}H_{9}$$

$$H_{11}C_5$$
  $O$   $O$   $O$   $C_5H_{11}$ 

Particularly preferred compounds from the group of the compounds of the sub-formulae I1 to I25 here are compounds in which the total number of C atoms in the two alkyl groups is in the range 4 to 6. These are the com-

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pounds I3 to I5, I7 to I9, I11 to I13, I16, I17 and I21. Particular preference is given here to the sub-formulae I8, I9, I12 and I13.

The liquid-crystalline medium particularly preferably comprises one, two or three compounds of the formula I.

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The proportion of compounds of the formula I in the mixture as a whole is 1 to 60% by weight, preferably 3 to 50% by weight and particularly preferably either 3 to 12% by weight (embodiment A) or 15 to 50% by weight (embodiment B).

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The compounds of the formula I are prepared by methods known per se, as described in the literature (for example in the standard works, such as Houben-Weyl, Methoden der organischen Chemie [Methods of Organic Chemistry], Georg-Thieme-Verlag, Stuttgart), to be precise under reaction conditions which are known and suitable for the said reactions. Use can also be made here of variants which are known per se, but are not mentioned here in greater detail.

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The compounds of the formula I are preferably prepared as described in EP 0 132 377 A2.

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The present invention also relates to electro-optical display devices (in particular STN or MLC displays having two plane-parallel outer plates, which, together with a frame, form a cell, integrated non-linear elements for switching individual pixels on the outer plates, and a nematic liquid-crystal mixture of positive dielectric anisotropy and high specific resistance which is located in the cell) which contain the media according to the invention, and to the use of these media for electro-optical purposes. Besides reflective applications, the mixtures according to the invention are also suitable for IPS (in plane switching) applications and OCB (optically controlled birefringence) applications.

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The liquid-crystal mixtures according to the invention enable a significant widening of the available parameter latitude.

The achievable combinations of rotational viscosity  $\gamma_1$  and optical anisotropy  $\Delta n$  are far superior to previous materials from the prior art.

The requirement for a high clearing point, nematic phase at low temperature, low rotational viscosity  $\gamma_1$  and high  $\Delta n$  has hitherto only been achieved to an inadequate extent. Although systems such as, for example, the mixture of Comparative Example 2, which is commercially available from Merck, have similar properties to the mixtures according to the invention, they have, however, significantly worse values for the rotational viscosity  $\gamma_1$ .

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Other mixture systems, such as, for example, the mixture of Comparative Example 1, which is commercially available from Merck, have comparable rotational viscosities  $\gamma_1$ , but have significantly worse values for the optical anisotropy  $\Delta n$ .

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The liquid-crystal mixtures according to the invention, while retaining the nematic phase down to -20°C, preferably down to -30°C and particularly preferably down to -40°C, enable clearing points above 65°C, preferably above 70°C and particularly preferably above 75°C, simultaneously dielectric anisotropy values  $\Delta\epsilon$  of  $\geq$  4, preferably  $\geq$  4.5, and a high value for the specific resistance to be achieved, enabling excellent STN and MLC displays to be obtained. In particular, the mixtures are characterised by low operating voltages. The TN thresholds are below 2.0 V, preferably below 1.9 V and particularly preferably below 1.8 V.

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The liquid-crystal mixtures according to the invention have optical anisotropies  $\Delta n$  which, in the case of embodiment A, are preferably  $\leq 0.100$  and particularly preferably  $\leq 0.095$ . In the case of embodiment B, the optical anisotropies are preferably  $\geq 0.160$ , particularly preferably  $\geq 0.180$  and in particular  $\geq 0.200$ .

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It goes without saying that, through a suitable choice of the components of the mixtures according to the invention, it is also possible for higher clearing points to be achieved at higher threshold voltages or lower clearing points to be achieved at lower threshold voltages with retention of the other advantageous properties. At viscosities correspondingly increased only slightly, it is likewise possible to obtain mixtures having greater  $\Delta\epsilon$  and thus lower thresholds. The MLC displays according to the invention preferably operate at the first Gooch and Tarry transmission minimum [C.H. Gooch and H.A. Tarry, Electron. Lett. 10, 2-4, 1974; C.H. Gooch and H.A. Tarry, Appl. Phys., Vol. 8, 1575-1584, 1975], where particularly favourable electro-optical properties, such as, for example, high steepness of the characteristic line and low angle dependence of the contrast (German Patent 30 22 818), are achieved. In addition, significantly higher specific resistances can be achieved using the mixtures according to the invention at the first minimum than in the case of mixtures comprising cyano compounds. Through a suitable choice of the individual components and their proportions by weight, the person skilled in the art is able to set the birefringence necessary for a pre-specified layer thickness of the MLC display using simple routine methods.

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The rotational viscosity  $\gamma_1$  of the mixtures according to the invention at  $20^{\circ}\text{C}$  is preferably  $\leq 180$  mPa·s, particularly preferably  $\leq 160$  mPa·s. In a specific embodiment (embodiment A), the rotational viscosity  $\gamma_1$  is particularly preferably  $\leq 80$  mPa·s and in particular  $\leq 70$  mPa·s. The ratio  $\gamma_1$  to  $(\Delta n)^2$  here is preferably  $\leq 8000$ , particularly preferably  $\leq 7000$ . In a specific embodiment (embodiment B), the ratio is particularly preferably  $\leq 5000$  and in particular  $\leq 4500$ . The nematic phase range is preferably at least  $90^{\circ}\text{C}$  and extends at least  $-20^{\circ}$  to  $+70^{\circ}\text{C}$ .

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Measurements of the capacity holding ratio (HR) [S. Matsumoto et al., Liquid Crystals 5, 1320 (1989); K. Niwa et al., Proc. SID Conference, San Francisco, June 1984, p. 304 (1984); G. Weber et al., Liquid Crystals 5, 1381 (1989)] have shown that mixtures according to the invention comprising compounds of the formula I exhibit a significantly smaller decrease in the HR with increasing temperature than analogous mixtures comprising

cyanophenylcyclohexanes of the formula

the formula 
$$R \leftarrow O \rightarrow C \rightarrow C \rightarrow CN$$

instead of the compounds of the for-

mula I according to the invention.

The UV stability of the mixtures according to the invention is also considerably better, i.e. they exhibit a significantly smaller decrease in the HR on exposure to UV.

Besides at least one compound of the formula I, the medium according to the invention additionally comprises one or more compounds selected from the group consisting of compounds of the general formulae II to X:

 $R^0 \xrightarrow{H} Q \xrightarrow{Y^1} X^0$ 

15  $R^0 \longrightarrow H \longrightarrow Z^0 \longrightarrow H \longrightarrow X^0$  III

 $R^{0} = H + Z^{0} +$ 

 $R^{0} \xrightarrow{H} O \xrightarrow{Y^{3}} V^{1}$ 

 $R^{0} - H - Z^{0} - O - X^{0}$  VI

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$$R^{0} \xrightarrow{H} C \xrightarrow{Y^{3}} Z^{0} \xrightarrow{Q^{1}} X^{0}$$

$$VII$$

$$R^0 \longrightarrow O \longrightarrow O \longrightarrow X^0$$
 VIII

$$R^{0} \longrightarrow Q^{5} \qquad Q^{0} \longrightarrow Q^{0} Q^{0$$

$$R^{0} \xrightarrow{Q^{5}} Q^{3} \xrightarrow{Q^{1}} Z^{0} \xrightarrow{Q^{2}} X^{0} \qquad \chi$$

in which the individual radicals have the following meanings:

R<sup>0</sup>: n-alkyl, oxaalkyl, fluoroalkyl or alkenyl, each having up to 9 C atoms;

X<sup>0</sup>: F, CI, halogenated alkyl or halogenated alkoxy having 1 to 6 C atoms, or halogenated alkenyl having 2 to 6 C atoms;

$$Z^0$$
:  $-CF_2O_-$ ,  $-OCF_2-$ ,  $-CH_2O_-$ ,  $-OCH_2-$ ,  $-COO_-$ ,  $-O-CO_-$ ,  $-CH=CH_-$ ,  $-C_2H_4-$ ,  $-C_2F_4-$ ,  $-CH_2CF_2-$ ,  $-CF_2CH_2-$  or  $-C_4H_8-$ ;

 $Y^1$ ,  $Y^2$ ,  $Y^3$ ,  $Y^4$ ,  $Y^5$  and  $Y^6$ : each, independently of one another, H or F;

35 r: 0 or 1, preferably 1.

The term "alkyl" covers straight-chain and branched alkyl groups having 1 to 9 carbon atoms, preferably the straight-chain groups methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl and nonyl. Groups having 1 to 5 carbon atoms are particularly preferred.

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The term "alkenyl" covers straight-chain and branched alkenyl groups having 2 to 9 carbon atoms, preferably the straight-chain groups having 2 to 7 carbon atoms. Particularly preferred alkenyl groups are C<sub>2</sub>-C<sub>7</sub>-1E-alkenyl, C<sub>4</sub>-C<sub>7</sub>-3E-alkenyl, C<sub>5</sub>-C<sub>7</sub>-4-alkenyl, C<sub>6</sub>-C<sub>7</sub>-5-alkenyl and C<sub>7</sub>-6-alkenyl, in particular C<sub>2</sub>-C<sub>7</sub>-1E-alkenyl, C<sub>4</sub>-C<sub>7</sub>-3E-alkenyl and C<sub>5</sub>-C<sub>7</sub>-4-alkenyl. Examples of preferred alkenyl groups are vinyl, 1E-propenyl, 1E-butenyl, 1E-pentenyl, 1E-hexenyl, 1E-heptenyl, 3-butenyl, 3E-pentenyl, 3E-hexenyl, 3E-heptenyl, 4-pentenyl, 4Z-hexenyl, 4E-hexenyl, 4Z-heptenyl, 5-hexenyl, 6-heptenyl and the like. Groups having up to 5 carbon atoms are particularly preferred.

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The term "fluoroalkyl" preferably covers straight-chain groups having a terminal fluorine, i.e. fluoromethyl, 2-fluoroethyl, 3-fluoropropyl, 4-fluorobutyl, 5-fluoropentyl, 6-fluorohexyl and 7-fluoroheptyl. However, other positions of the fluorine are not excluded.

The term "oxaalkyl" preferably covers straight-chain radicals of the formula  $C_nH_{2n+1}$ -O-(CH<sub>2</sub>)<sub>m</sub>, in which n and m each, independently of one another, denote 1 to 6. Preferably, n = 1 and m = 1 to 6.

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In the formulae II to X,

$$Y^1$$
 preferably denotes  $O - F$ ,  $O -$ 

The compound of the formula II is preferably

$$R^0 \longrightarrow H \longrightarrow O \longrightarrow X^0$$

$$R^0 \longrightarrow H \longrightarrow C \longrightarrow X^0$$

$$R^{0} \xrightarrow{H} \xrightarrow{H} O \xrightarrow{F} X^{0} \qquad IIc$$

in which R<sup>0</sup> and X<sup>0</sup> can adopt the meanings indicated above. Preferably, however, R<sup>0</sup> is n-alkyl or alkenyl having up to 9 C atoms, particularly preferably n-alkyl having 1 to 5 C atoms or alkenyl having 2 to 5 C atoms, and X<sup>0</sup> is F, OCF<sub>3</sub>, CF<sub>3</sub> or OCHF<sub>2</sub>.

The compound of the formula III is preferably

$$R^0$$
  $H$   $O$   $X^0$  Illa

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in which  $R^0$  and  $X^0$  can adopt the meanings indicated above. Preferably, however,  $R^0$  is n-alkyl or alkenyl having up to 9 C atoms, particularly preferably n-alkyl having 1 to 5 C atoms or alkenyl having 2 to 5 C atoms, and  $X^0$  is F, OCF<sub>3</sub>, CF<sub>3</sub> or OCHF<sub>2</sub>.

5 The compound of the formula IV is preferably

$$R^0 \longrightarrow H \longrightarrow CF_2O \longrightarrow CF_2O \longrightarrow F$$
 IVa

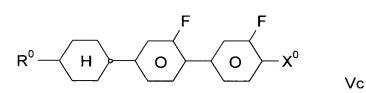
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$$R^0 \longrightarrow H \longrightarrow COO \longrightarrow COO \longrightarrow F$$
 IVb

in which  $R^0$  and  $X^0$  can adopt the meanings indicated above. Preferably, however,  $R^0$  is n-alkyl having up to 9 C atoms, particularly preferably n-alkyl having 1 to 5 C atoms, and  $X^0$  is F, OCF<sub>3</sub>, CF<sub>3</sub> or OCHF<sub>2</sub>, particularly preferably F.

The compound of the formula V is preferably

$$R^0 \longrightarrow H \longrightarrow O \longrightarrow X^0$$
 Va

$$R^0$$
  $H$   $O$   $F$   $V_b$ 



 $R^{0} \longrightarrow H \longrightarrow O \longrightarrow K^{0} \longrightarrow K^{0}$ 15

$$R^0$$
 $H$ 
 $O$ 
 $F$ 
 $F$ 
 $F$ 
 $Vf$ 

in which R<sup>0</sup> and X<sup>0</sup> can adopt the meanings indicated above. Preferably, however, R<sup>0</sup> is n-alkyl having up to 9 C atoms, particularly preferably n-alkyl having 1 to 5 C atoms, and X<sup>0</sup> is F, OCF<sub>3</sub>, CF<sub>3</sub> or OCHF<sub>2</sub>, particularly preferably F. Particular preference is given to the formula Vc.

The compound of the formula VII is preferably

$$R^0 \longrightarrow H$$
  $O \longrightarrow COO \longrightarrow COO \longrightarrow K^0$  VIIa

$$R^0 \longrightarrow H \longrightarrow COO \longrightarrow X^0$$
 VIIIb

in which R<sup>0</sup> and X<sup>0</sup> can adopt the meanings indicated above. Preferably, however, R<sup>0</sup> is n-alkyl having up to 9 C atoms, particularly preferably n-alkyl having 1 to 5 C atoms, and X<sup>0</sup> is F, OCF<sub>3</sub>, CF<sub>3</sub> or OCHF<sub>2</sub>.

The compound of the formula VIII is preferably

$$R^{0} \longrightarrow O \longrightarrow F \qquad F$$

$$VIIIa$$

in which R<sup>0</sup> and X<sup>0</sup> can adopt the meanings indicated above. Preferably, however, R<sup>0</sup> is n-alkyl having up to 9 C atoms, particularly preferably n-alkyl having 1 to 5 C atoms, and X<sup>0</sup> is F, OCF<sub>3</sub>, CF<sub>3</sub> or OCHF<sub>2</sub>, particularly preferably F.

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The compound of the formula X is preferably

$$R^0 \longrightarrow O \longrightarrow CF_2O \longrightarrow F$$
 $K^0 \longrightarrow K$ 
 $K^$ 

in which R<sup>0</sup> and X<sup>0</sup> can adopt the meanings indicated above. Preferably, however, R<sup>0</sup> is n-alkyl having up to 9 C atoms, particularly preferably n-alkyl having 1 to 5 C atoms, and X<sup>0</sup> is F, OCF<sub>3</sub>, CF<sub>3</sub> or OCHF<sub>2</sub>, particularly preferably F.

Particularly preferred embodiments are indicated below.

- The medium comprises one or more compounds of the formulae II, III, IV, V, VI, VII, VIII, IX and/or X, preferably one or more compounds of the formulae IIa, IIb, IIc, IIIa, IVa, IVb, Vc, VIIa, VIIb, VIIIa, VIIIb and/or Xa.
- The proportion of compounds of the formulae II to X in the mixture as a whole is 20 to 70% by weight, preferably 30 to 60% by weight and particularly preferably 35 to 55% by weight.
- The proportion of compounds of the formulae I to X together in the mixture as a whole is at least 30% by weight, preferably at least 40% by weight and particularly preferably at least 50% by weight.
- The medium essentially consists of compounds of the formulae I to X.
  - The I: (II + III + IV + V + VI + VIII + IX + X) weight ratio is preferably in the range from 1: 10 to 10: 1.

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The optimum mixing ratio of the compounds of the formulae I and II + III + IV + V + VI + VIII + IX + X depends substantially on the desired properties, on the choice of the components of the formulae I, II, III, IV, V, VI, VII, VIII, IX and/or X and on the choice of any other components present. Suitable mixing ratios within the ranges indicated above can easily be determined from case to case.

Besides at least one compound of the formula I and at least one compound selected from the group consisting of compounds of the general formulae II to X, the medium according to the invention additionally comprises one or more compounds selected from the group consisting of compounds of the general formulae XI to XVII:

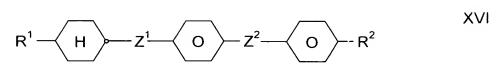
$$R^1 - H - Z^1 - H - R^2$$

$$R^1 \longrightarrow R^2$$
 XII

$$R^{1} \longrightarrow O \longrightarrow Z^{1} \longrightarrow O \longrightarrow R^{2}$$
 XIII

$$R^{1} - H - Z^{1} - H - R^{2}$$
 XIV

$$R^{1} - \left(H\right) - Z^{1} - \left(H\right) - Z^{2} - \left(O\right) - R^{2}$$



 $R^{1} - O - Z^{1} - O - R^{2}$  XVII

in which the individual radicals have the following meanings:

10
R¹ and R²: independently of one another, identically or differently,
n-alkyl, n-alkoxy or alkenyl, each having up to 9 C atoms; and

 $Z^1$  and  $Z^2$ : independently of one another, identically or differently, a single bond,  $-CF_2O_-$ ,  $-OCF_2-$ ,  $-CH_2O_-$ ,  $-OCH_2-$ ,  $-COO_-$ ,  $-O-CO_-$ ,  $-CH=CH_-$ ,  $-C_2H_4-$ ,  $-C_2F_4-$ ,  $-CH_2CF_2-$ ,  $-CF_2CH_2-$  or  $-C_4H_8-$ , preferably each a single bond.

The compound of the formula XI is preferably

 $R^1 \longrightarrow H \longrightarrow R^2$  XIa

 $R^1$  H  $R^2$  XIb

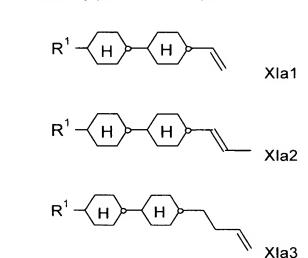
in which R<sup>1</sup> and R<sup>2</sup> can adopt the meanings indicated above. Preferably, however, R<sup>1</sup> is n-alkyl or alkenyl having up to 9 C atoms, particularly preferably n-alkyl having 1 to 5 C atoms or alkenyl having 2 to 5 C atoms, and R<sup>2</sup> is alkenyl having up to 9 C atoms, particularly preferably alkenyl having 2 to 5 C atoms.

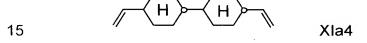
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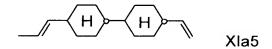
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Particularly preferred compounds of the formula XIa are







in which R<sup>1</sup> can adopt the meanings indicated above, but preferably denotes n-alkyl having 1 to 5 C atoms.

The compounds of the formulae XIa1 and XIa2 are particularly preferred.

The compound of the formula XII is preferably

$$R^1$$
  $H$   $O$   $R^2$ 

in which  $R^1$  and  $R^2$  can adopt the meanings indicated above. Preferably, however,  $R^1$  is n-alkyl having up to 9 C atoms, particularly preferably n-alkyl having 1 to 5 C atoms, and  $R^2$  is alkoxy having up to 9 C atoms, particularly preferably alkoxy having 1 to 5 C atoms.

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The compound of the formula XIII is preferably

$$R^1 \longrightarrow O \longrightarrow R^2$$
 XIIIa

in which R<sup>1</sup> and R<sup>2</sup> can adopt the meanings indicated above. Preferably, however, R<sup>1</sup> is n-alkyl having up to 9 C atoms, particularly preferably n-alkyl having 1 to 5 C atoms, and R<sup>2</sup> is alkenyl having up to 9 C atoms, particularly preferably alkenyl having 2 to 5 C atoms.

The compound of the formula XV is preferably

$$R^1 \longrightarrow H \longrightarrow O \longrightarrow R^2$$
 XVa

in which R<sup>1</sup> and R<sup>2</sup> can adopt the meanings indicated above. Preferably, however, R<sup>1</sup> is alkenyl having up to 9 C atoms, particularly preferably alkenyl having 2 to 5 C atoms, and R<sup>2</sup> is n-alkyl having up to 9 C atoms, particularly preferably n-alkyl having 1 to 5 C atoms.

Particularly preferred embodiments are indicated below.

- The medium comprises one or more compounds of the formulae XI,
   XII, XIII, XIV, XV, XVI and/or XVII, preferably one or more compounds of the formulae XIa, XIb, XIIa, XIIIa and/or XVa.
- The proportion of compounds of the formulae XI to XVII in the mixture as a whole is 5 to 70% by weight, preferably 10 to 60% by weight and particularly preferably either 10 to 30% by weight (embodiment B) or 35 to 55% by weight (embodiment A).
- The proportion of compounds of the formulae I to XVII together in the mixture as a whole is at least 50% by weight, preferably at least 70% by weight and particularly preferably at least 90% by weight.

 The medium essentially consists of compounds of the formulae I to XVII.

The total amount of compounds of the formulae I to XVII in the mixtures according to the invention is not crucial. The mixtures may therefore comprise one or more further components in order to optimise various properties. However, the observed effect on the rotational viscosity and the optical anisotropy is generally greater the higher the total concentration of compounds of the formulae I to XVII.

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Furthermore, the medium according to the invention may additionally comprise one or more compounds selected from compounds of the general formula XVIII:

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$$R^1 \longrightarrow H \longrightarrow O \longrightarrow H \longrightarrow R^2$$
 XVIII

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in which R<sup>1</sup> and R<sup>2</sup> can adopt the meanings indicated above. Preferably, however, R<sup>1</sup> and R<sup>2</sup> denote n-alkyl having up to 9 C atoms, particularly preferably n-alkyl having 1 to 5 C atoms.

The proportion of compounds of the formula XVIII in the mixture as a whole can be up to 10% by weight.

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In addition, the medium according to the invention may additionally comprise one or more compounds selected from the group consisting of compounds of the general formulae XIX to XXVI:

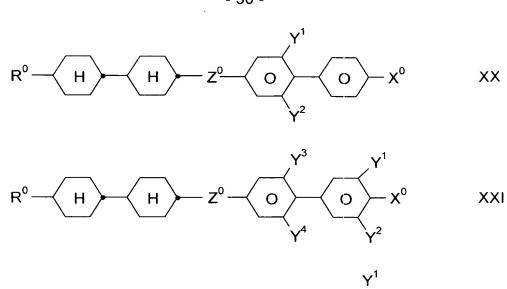
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$$R^0 \longrightarrow H \longrightarrow Z^0 \longrightarrow O \longrightarrow X^1$$
 XIX

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 $R^{0} \xrightarrow{H} Z^{0} \xrightarrow{H} \xrightarrow{H} O \xrightarrow{\chi^{0}} X^{0} \qquad XXIII$ 

$$R^0 \longrightarrow H \longrightarrow Z^0 \longrightarrow H \longrightarrow Q^2$$
 XXIII

 $R^0 \longrightarrow H \longrightarrow H \longrightarrow Z^0 \longrightarrow X^0 \qquad XXIV$ 

$$R^0 \longrightarrow H \longrightarrow O \longrightarrow X^0 \longrightarrow XXV$$

$$R^0 \longrightarrow H \longrightarrow O \longrightarrow H \longrightarrow X^0$$
 XXVI

in which  $R^0$ ,  $X^0$ ,  $Y^1$ ,  $Y^2$ ,  $Y^3$ ,  $Y^4$  and  $Z^0$  each, independently of one another, have one of the meanings indicated above. Preferably,  $X^0$  is F, CI, CF<sub>3</sub>, OCF<sub>3</sub> or OCHF<sub>2</sub>.  $R^0$  preferably denotes alkyl, oxaalkyl, fluoroalkyl or alkenyl, each having up to 6 C atoms, and  $Z^0$  preferably denotes a single bond or -CH<sub>2</sub>-CH<sub>2</sub>-.  $Y^1$ ,  $Y^2$ ,  $Y^3$  and  $Y^4$  each, independently of one another, denote H or F.

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The individual compounds of the formulae II to XXVI and their sub-formulae which can be used in the media according to the invention are either known or can be prepared analogously to known compounds.

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It has been found that even a relatively small proportion of compounds of the formula I mixed with conventional liquid-crystal materials, but in particular with one or more compounds of the formulae II, III, IV, V, VI, VII, VIII, IX and/or X, results in a significant reduction in the rotational viscosity  $\gamma_1$  and in higher values for the optical anisotropy  $\Delta n$ , enabling shorter response times of the displays to be achieved, with broad nematic phases having low smectic-nematic transition temperatures being observed at the same time, causing an improvement in the storage stability. The compounds of the formulae I to X are colourless, stable and readily miscible with one another and with other liquid-crystal materials. The mixtures according to the invention are furthermore distinguished by very high clearing points.

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The construction of the MLC display according to the invention from polarisers, electrode base plates and electrodes having a surface treatment corresponds to the conventional design for displays of this type. The term conventional design here is broadly drawn and also covers all derivatives

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and modifications of the MLC display, in particular also matrix display elements based on poly-Si TFT or MIM.

An essential difference between the displays according to the invention and the hitherto conventional displays based on the twisted nematic cell consists, however, in the choice of the liquid-crystal parameters of the liquid-crystal layer.

The liquid-crystal mixtures which can be used in accordance with the invention are prepared in a manner conventional per se. In general, the desired amount of the components used in lesser amount is dissolved in the components making up the principal constituent, preferably at elevated temperature. It is also possible to mix solutions of the components in an organic solvent, for example in acetone, chloroform or methanol, and to remove the solvent again, for example by distillation, after mixing.

The dielectrics may also comprise further additives known to the person skilled in the art and described in the literature. For example, 0 to 15% of pleochroic dyes or chiral dopants may be added.

In the present application and in the following examples, the structures of the liquid-crystal compounds are indicated by means of acronyms, with the transformation into chemical formulae taking place in accordance with Tables A and B below. All radicals C<sub>n</sub>H<sub>2n+1</sub> and C<sub>m</sub>H<sub>2m+1</sub> are straight-chain alkyl radicals having n and m C atoms respectively; n and m preferably denote 0, 1, 2, 3, 4, 5, 6 or 7. The coding in Table B is self-evident. In Table A, only the acronym for the parent structure is indicated. In individual cases, the acronym for the parent structure is followed, separated by a dash, by a code for the substituents R<sup>1</sup>, R<sup>2</sup>, L<sup>1</sup> and L<sup>2</sup>.

Code for  $R^1$ ,  $R^2$ ,  $L^1$ ,  $L^2$   $R^1$   $R^2$   $L^1$   $L^2$  nm  $C_nH_{2n+1}$   $C_mH_{2m+1}$  H H

	nOm	$C_nH_{2n+1}$	$OC_mH_{2m+1}$	Н	Н
	nO.m	$OC_nH_{2n+1}$	$C_mH_{2m+1}$	Н	Н
	n	$C_nH_{2n+1}$	CN	Н	Н
	nN.F	$C_nH_{2n+1}$	CN	Н	F
5	nF	$C_nH_{2n+1}$	F	Н	Н
	nOF	$OC_nH_{2n+1}$	F	Н	Н
	nCl	$C_nH_{2n+1}$	CI	Н	Н
	nF.F	$C_nH_{2n+1}$	F	Н	F
	nF.F.F	$C_nH_{2n+1}$	F	F	F
10	nCF <sub>3</sub>	$C_nH_{2n+1}$	CF <sub>3</sub>	Н	H
	$nOCF_3$	$C_nH_{2n+1}$	OCF <sub>3</sub>	Н	Н
	nOCF <sub>2</sub>	$C_nH_{2n+1}$	OCHF <sub>2</sub>	Н	Н
	nS	$C_nH_{2n+1}$	NCS	Н	Н
15	rVsN	$C_rH_{2r+1}$ - $CH=CH-C_sH_{2s}$ -	CN	Н	Н
	rEs <b>N</b>	$C_rH_{2r+1}$ -O- $C_sH_{2s}$ -	CN	Н	Н
	nAm	$C_nH_{2n+1}$	$COOC_mH_{2m+1}$	Н	Н
	nOCCF <sub>2</sub> .F.F	$C_nH_{2n+1}$	OCH <sub>2</sub> CF <sub>2</sub> H	F	F
20	V-n	CH <sub>2</sub> =CH	$C_nH_{2n+1}$	Н	Н

Preferred mixture components of the mixture concept according to the invention are shown in Tables A and B:

### Table A:

$$R^{1} \xrightarrow{O}_{N} \xrightarrow{O}_{L^{2}} R^{2}$$

PYP

$$R^{1} \longrightarrow O_{N} \longrightarrow O_{L^{2}}^{L^{1}}$$

**PYRP** 

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$$R^{1} \longrightarrow H \longrightarrow O \longrightarrow C$$

$$L^{2}$$

20 BCH

$$R^1$$
  $H$   $O$   $O$   $H$   $R^2$ 

CBC

$$R^{1}$$
  $H$   $H$   $R^{2}$   $CCH$ 

$$R^{1} \longrightarrow H \longrightarrow L^{2}$$

$$CCP$$

$$R^1$$
  $H$   $O$   $C \equiv C$   $O$   $C$   $C$ 

**CPTP** 

CEPTP

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$$R^{1} - \left( H \right) - C_{2}H_{4} - \left( O \right) - C \equiv C - \left( O \right) + \left( C \right)$$

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$$R^1 - H - C_2H_4 - O + R^2$$

15 ECCP

$$R^1$$
  $C_2H_4$   $H$   $O$   $C_2$ 

<sup>20</sup> CECP

25 
$$R^1 - H - (C_2H_4)_2 - O + R^2$$

CCEEP

$$R^{1} - \left( C_{2}H_{4}\right)_{2} - \left( H \right) - \left( C_{2}H_{4}\right)_{2}$$

CEECP

$$R^1 \longrightarrow C_2H_4 \longrightarrow C_2^1$$

## **EPCH**

PCH

$$R^{1} \xrightarrow{H} O \xrightarrow{L^{2}} R^{2}$$

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$$R^{1} - \underbrace{O} - C = C - \underbrace{O}_{L^{2}}^{L^{1}} R^{2}$$

15 **PTP** 

$$R^1 - C_2H_4 - O - C_2H_4$$

20 BECH

$$R^1 \longrightarrow C_2H_4 \longrightarrow C_2^L$$

25 **EBCH** 

$$R^1$$
  $O$   $H$   $R^2$   $CPC$ 

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$$R^1$$
  $O$   $O$   $R^2$   $C$ 

35 B

$$R^1 - O - C_2H_4 - O - R^2$$

FET

$$R^{1} - H - O + R^{2}$$

$$CGG$$

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$$R^1$$
  $\longrightarrow$   $O$   $\longrightarrow$   $C$   $\longrightarrow$   $C$ 

CGU

CFU

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$$R^1$$
  $H$   $O$   $F$   $R^2$ 

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Table B:

$$25 \qquad C_nH_{2n+1} \longrightarrow H \longrightarrow O \longrightarrow O-C_mH_{2m+1}$$

#### PCH-nOm

$$C_nH_{2n+1}$$
  $H$   $O$   $F$ 

BCH-nF.F

$$C_nH_{2n+1}$$
  $H$   $O$   $F$   $F$ 

## CFU-n-F

$$C_{n}H_{2n+1} - C_{2}H_{4} - O - C_{m}H_{2m+1}$$

#### Inm

$$C_{n}H_{2n+1} - H - O - H - C_{m}H_{2m+1}$$

### CBC-nmF

$$C_nH_{2n+1} \longrightarrow O \longrightarrow CN$$

#### PDX-n

$$20 \qquad C_nH_{2n+1} \longrightarrow H \longrightarrow COO \longrightarrow F$$

### CCZU-n-F

$$C_nH_{2n+1}$$
 O O CN

### K3n

$$C_nH_{2n+1}$$
  $O$   $O$   $C_mH_{2m}$   $CH_2$ 

#### PP-n-mV1

$$C_nH_{2n+1}$$
  $H$   $C_2H_4$   $O$   $C_mH_{2m+1}$ 

35 ECCP-nm

$$C_nH_{2n+1}$$
  $H$   $C_2H_4$   $O$   $F$ 

5 ECCP-nF.F.F

$$C_nH_{2n+1}$$
  $H$   $C_mH_{2m+1}$ 

### CCH-nm

 $C_nH_{2n+1} - H - CH_2O-C_mH_{2m+1}$ 

### CCH-n1Em

15 
$$C_nH_{2n+1}$$
  $O$   $O$   $O$   $C_mH_{2m+1}$ 

PGP-n-m

$$C_{n}H_{2n+1} \longrightarrow O \longrightarrow O \longrightarrow F$$

PGIGI-n-F

PGIGI-n-CI

$$C_nH_{2n+1} \longrightarrow O \longrightarrow O \longrightarrow F$$

GGP-n-F

$$C_nH_{2n+1}$$
  $O$   $O$   $O$   $O$   $O$   $O$ 

GGP-n-CI

$$C_nH_{2n+1} - H - O - F$$

CGU-n-F

$$C_{n}H_{2n+1} - H - O O F$$

CDU-n-F

$$C_{n}H_{2n+1} - H - O - F$$

CGG-n-F

$$C_{n}H_{2n+1} - H - CF_{2}CF_{2} - H - C_{m}H_{2m+1}$$

### CWC-n-m

$$25 \qquad C_nH_{2n+1} \longrightarrow H \longrightarrow CF_3$$

### CCH-nCF<sub>3</sub>

$$C_nH_{2n+1} \longrightarrow H \longrightarrow F \longrightarrow F$$

CUP-nF.F

$$C_nH_{2n+1}$$
  $H$   $H$ 

CC-n-V

#### CWCC-n-m

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$$C_nH_{2n+1}$$
  $O$   $CF_2O$   $F$ 

#### PQU-n-F

### CCG-V-F

$$C_{n}H_{2n+1} \xrightarrow{\qquad \qquad H} \xrightarrow{\qquad \qquad } O \xrightarrow{\qquad \qquad } OCF_{3}$$

### CCU-n-OT

$$C_{n}H_{2n+1} \xrightarrow{H} CF_{2}O \xrightarrow{O} F$$

### CCQU-n-F

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$$C_nH_{2n+1}$$
  $H$   $CF_2O$   $O$   $O$   $OCF_3$ 

$$C_nH_{2n+1}$$
  $O$   $F$ 

Dec-U-n-F

 $C_{n}H_{2n+1} - H - O = O + F$ 

CPTU-n-F

$$C_nH_{2n+1}$$
  $O$   $F$   $O$   $F$ 

15 **GPTU-n-F** 

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$$C_nH_{2n+1}$$
  $O$   $O$   $F$   $O$   $F$ 

20 - **PGU-n-F** 

$$C_nH_{2n+1}$$
  $H$   $H$ 

25 **CC-n-V1** 

CC-V-V1

$$C_nH_{2n+1}$$
  $H$   $O$   $OCF_3$ 

## CCP-nOCF<sub>3</sub>

$$C_{n}H_{2n+1} - H - O - OCF_{3}$$

## CCP-nOCF<sub>3</sub>.F

$$C_{n}H_{2n+1} - H + O + F$$

#### CCP-nF.F.F

15 
$$C_nH_{2n+1}$$
  $H$   $O$   $COO$   $O$   $OCF$ 

#### CGZP-n-OT

### CCP-V-m

$$\begin{array}{c|c} & & & \\ & & & \\ & & & \\ \end{array} \begin{array}{c} & & \\ \end{array} \begin{array}{c} & & \\ & & \\ \end{array} \begin{array}{c} & & \\ \end{array} \begin{array}{c} & & \\ & \\ \end{array} \begin{array}{c} & & \\ \end{array} \begin{array}{c} & & \\ & \\ \end{array} \begin{array}{c} & & \\ & \\ \end{array} \begin{array}{c} & \\ \end{array} \begin{array}{c} & &$$

## CCP-V2-m

$$C_nH_{2n+1}$$

Nap-U-n-F

$$C_nH_{2n+1}$$
  $H$   $O$   $COO$   $F$ 

#### CPZU-n-F

$$C_{n}H_{2n+1} - H - CF_{2}CF_{2}CF_{3}$$

## CC-n-DDT

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$$C_nH_{2n+1}$$
 H OCHFCF<sub>3</sub>

#### CC-n-OMT

$$C_{n}H_{2n+1} \longrightarrow O \longrightarrow CN$$

#### DU-n-N

$$C_{n}H_{2n+1} \longrightarrow H \longrightarrow CF_{2}CF_{2} \longrightarrow H \longrightarrow G$$

#### CWCU-n-F

#### CWCG-n-OT

$$C_{n}H_{2n+1} - H - CH_{2}O - H - C_{m}H_{2m+1}$$

#### CCOC-n-m

$$C_nH_{2n+1}$$
 $H$ 
 $C_2F_4$ 
 $O$ 
 $F$ 

#### CCWU-n-F

 $C_{n}H_{2n+1} - H - CF_{2}O - O - COO - F$ 

CQUZU-n-F

10  $C_{n}H_{2n+1} - H - CF_{2}O - O - F$ 

15 CCQUZG-n-F

20 CCQUZP-n-OT

$$C_nH_{2n+1}$$
  $-CF_2O$   $-COO$   $-COO$   $-OCF_3$ 

25 CQUZG-n-OT

$$C_nH_{2n+1}$$
  $H$ 

CVC-n-V

$$C_nH_{2n+1}$$
 $H$ 
 $O$ 
 $OCF_3$ 

CVCP-nV-OT

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- 46 -

$$C_nH_{2n+1}$$
  $O$   $CF_2O$   $F$   $F$ 

PUQU-n-F

$$C_nH_{2n+1}$$
  $O$   $O$   $C_2H_4$   $O$   $CI$ 

FET-nCl

#### Table C:

Table C shows possible dopants which are preferably added to the mixtures according to the invention.

C 15

**CB 15** 

CM 21

25 **R/S-811** 

$$C_3H_7$$
  $H$   $H$   $O$   $CH_2$   $CH_5$   $CH_3$ 

30 CM 44

35 **CM 45** 

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**CM 47** 

$$C_5H_{11} \hspace{1cm} H \hspace{1cm} O \hspace{-0.5cm} - \hspace{-0.5cm} COO-CH_2-CH-OOC \hspace{-0.5cm} O \hspace{-0.5cm} H \hspace{-0.5cm} - \hspace{-0.5cm} C_5H_1$$

R/S-1011

$$C_3H_7$$
 $H$ 
 $H$ 
 $O$ 
 $O$ 
 $O$ 

R/S-3011

$$H_3C$$
 $H_3C$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 

CN

$$C_5H_{11} \xrightarrow{O} \xrightarrow{O} \xrightarrow{F} CH_3 \\ O \xrightarrow{\star} OCH-C_6H_{13}$$

R/S-4011

$$C_3H_7$$
 $H$ 
 $H$ 
 $O$ 
 $C_6H_{13}$ 
 $C_8H_{13}$ 

R/S-2011

#### Table D:

Stabilisers which can be added, for example, to the mixtures according to the invention are mentioned below.

$$HO \longrightarrow O \longrightarrow CH_2 \longrightarrow O \longrightarrow OH$$

$$C_nH_{2n+1}$$
  $H$   $O$   $OH$ 

НО

Besides one or more compounds of the formula I, particularly preferred mixtures comprise one, two, three, four, five or more compounds from Table B.

The following examples are intended to explain the invention without restricting it. Above and below, percentage data denote per cent by weight. All temperatures are indicated in degrees Celsius. cl.p. denotes clearing point.

Δn denotes the optical anisotropy (589 nm, 20°C). The optical data were measured at 20°C, unless expressly stated otherwise. Δε denotes the dielectric anisotropy ( $\Delta \epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$ , where  $\epsilon_{\parallel}$  denotes the dielectric constant parallel to the longitudinal molecular axes and  $\epsilon_{\perp}$  denotes the dielectric constant perpendicular thereto). The electro-optical data were measured in a TN cell at the 1st minimum (i.e. at a d ·  $\Delta$ n value of 0.5 μm) at 20°C, unless expressly stated otherwise. The rotational viscosity  $\gamma_1$  (mPa·s) was determined at 20°C.

 $V_{10}$  denotes the threshold voltage, i.e. the characteristic voltage at a relative contrast of 10%,  $V_{50}$  denotes the characteristic voltage at a relative contrast of 50% and  $V_{90}$  denotes the characteristic voltage at a relative contrast of 90%.  $V_0$  denotes the capacitive threshold voltage. The twist is 90°, unless indicated otherwise.

The elastic constants  $K_1$  and  $K_3$  were determined at 20°C.  $K_3/K_1$  is the ratio of the elastic constants  $K_3$  and  $K_1$ .

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#### Example 1

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CCP-20CF <sub>3</sub>	2.0%	Clearing point [°C]:	80.0
CCP-30CF <sub>3</sub>	8.0%	∆n [589 nm, 20°C]:	0.0934
CCZU-3-F	14.0%	Δε [1 kHz, 20°C]:	6.0
CC-3-V1	10.0%	y <sub>1</sub> [mPa·s, 20°C]:	70
PCH-301	7.0%	V <sub>10</sub> [V]:	1.64
CCP-V-1	12.0%	V <sub>50</sub> [V]:	1.99
CCG-V-F	10.0%	V <sub>90</sub> [V]:	2.48
CC-4-V	18.0%	V <sub>90</sub> /V <sub>10</sub> :	1.509
PUQU-2-F	6.0%		
PUQU-3-F	8.0%		
PGP-2-3	5.0%		

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### Example 2

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CCP-20CF <sub>3</sub>	4.0%	Clearing point [°C]:	79.0
CCP-30CF <sub>3</sub>	8.0%	∆n [589 nm, 20°C]:	0.0960
CCZU-3-F	14.0%		
CC-3-V1	10.0%		
PCH-301	9.0%		
CCP-V-1	16.0%		
CC-4-V	18.0%		
PUQU-1-F	8.0%		
PUQU-2-F	7.0%		
PGP-3-2	6.0%		

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CCP-20CF <sub>3</sub>	2.0%	Clearing point [°C]:	81.5
CCP-30CF <sub>3</sub>	8.0%	Δn [589 nm, 20°C]:	0.0940
CCZU-3-F	14.0%	Δε [1 kHz, 20°C]:	6.2
CC-3-V1	10.0%	γ <sub>1</sub> [mPa·s, 20°C]:	70
PCH-301	6.0%	V <sub>10</sub> [V]:	1.67
CCP-V-1	13.0%	V <sub>50</sub> [V]:	2.02
CCG-V-F	10.0%	V <sub>90</sub> [V]:	2.53
CC-4-V	18.0%	V <sub>90</sub> /V <sub>10</sub> :	1.512
PUQU-1-F	8.0%		
PUQU-2-F	6.0%		
PGP-3-2	5.0%		

15 <u>Example 4</u>

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CCP-30CF <sub>3</sub>	8.0%	Clearing point [°C]:	82.0
CCZU-3-F	13.0%	Δn [589 nm, 20°C]:	0.0925
CC-3-V1	10.0%	Δε [1 kHz, 20°C]:	6.1
CCP-V-1	13.0%		
CCG-V-F	10.0%		
CC-4-V	18.0%		
PUQU-1-F	8.0%		
PUQU-2-F	7.0%		
PGP-3-2	5.0%		
CVC-3-V	8.0%		

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PGU-2-F	2.0%	Clearing point [°C]:	80.5
CCP-20CF <sub>3</sub>	7.0%	Δn [589 nm, 20°C]:	0.0942
CCP-30CF <sub>3</sub>	7.0%	V <sub>10</sub> [V]:	1.65
CCZU-3-F	14.0%		
CC-3-V1	10.0%		
PCH-301	3.0%		
CCP-V-1	10.0%		
CCG-V-F	10.0%		
CC-4-V	18.0%		
PUQU-2-F	6.0%		
PUQU-3-F	8.0%		
PGP-2-4	5.0%		

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### Example 6

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PGU-2-F	7.0%	Clearing point [°C]:	79.0
CC-3-V1	10.0%	Δn [589 nm, 20°C]:	0.1036
CCP-V-1	12.0%	Δε [1 kHz, 20°C]:	5.0
CCP-V2-1	3.0%	γ₁ [mPa⋅s, 20°C]:	67
CCG-V-F	10.0%	V <sub>10</sub> [V]:	1.78
CCP-20CF <sub>3</sub>	4.0%	V <sub>50</sub> [V]:	2.13
CCP-30CF <sub>3</sub>	4.0%	V <sub>90</sub> [V]:	2.65
CCP-40CF <sub>3</sub>	2.0%	V <sub>90</sub> /V <sub>10</sub> :	1.490
CCZU-3-F	5.0%		
PCH-301	8.0%		
CC-4-V	18.0%		
PUQU-2-F	4.0%		**
PUQU-3-F	5.0%		
PGP-2-4	8.0%		

CC-4-V 18.0% Clearing point [°C]: 79.5 CC-3-V1 ∆n [589 nm, 20°C]: 11.0% 0.0939 PCH-302 Δε [1 kHz, 20°C]: 9.0% 6.0 5 CCP-20CF<sub>3</sub> γ<sub>1</sub> [mPa·s, 20°C]: 7.5% 71 CCP-30CF<sub>3</sub> V<sub>10</sub> [V]: 8.0% 1.80 CCZU-3-F 13.0%  $V_{50}$  [V]: 2.15 PGP-2-3 V<sub>90</sub> [V]: 5.5% 2.65  $V_{90}/V_{10}$ : PGP-2-4 5.0% 1.474 10 CCQU-2-F 6.0% CCQU-3-F 10.0% PUQU-2-F 3.0%

4.0%

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#### Example 8

PUQU-3-F

CCP-20CF <sub>3</sub>	4.0%	Clearing point [°C]:	79.0
CCP-30CF <sub>3</sub>	4.0%	∆n [589 nm, 20°C]:	0.0927
CCP-40CF <sub>3</sub>	4.0%	Δε [1 kHz, 20°C]:	5.1
CCZU-3-F	9.0%	γ <sub>1</sub> [mPa·s, 20°C]:	65
CC-3-V1	10.0%	V <sub>10</sub> [V]:	1.76
PCH-301	9.0%	V <sub>50</sub> [V]:	2.13
CCP-V-1	14.0%	V <sub>90</sub> [V]:	2.66
CCG-V-F	10.0%	V <sub>90</sub> /V <sub>10</sub> :	1.513
CC-4-V	18.0%		
PUQU-2-F	6.0%		
PUQU-3-F	7.0%		
PGP-2-3	5.0%		

CCP-30CF <sub>3</sub>	7.0%	Clearing point [°C]:	79.5
CCZU-2-F	2.0%	Δn [589 nm, 20°C]:	0.0947
CCZU-3-F	14.0%	Δε [1 kHz, 20°C]:	6.0
PUQU-2-F	6.0%	γ <sub>1</sub> [mPa·s, 20°C]:	68
PUQU-3-F	8.0%	V <sub>10</sub> [V]:	1.72
CCP-V-1	8.0%		
CC-3-V1	12.0%		
CC-4-V	18.0%		
PCH-301	10.0%		
PGP-2-3	6.0%	·	
CVCP-1V-OT	9.0%		

### Example 10

CCZU-2-F	3.0%	Clearing point [°C]:	79.0
CCZU-3-F	14.0%	Δn [589 nm, 20°C]:	0.0935
PCH-302	10.0%	Δε [1 kHz, 20°C]:	6.1
CCP-V-1	9.0%	γ <sub>1</sub> [mPa·s, 20°C]:	70
CCG-V-F	5.0%	V <sub>10</sub> [V]:	1.67
CC-3-V1	12.0%		
CC-4-V	18.0%		
PUQU-2-F	6.0%		
PUQU-3-F	8.0%		
PGP-2-3	5.0%		
CVCP-1V-OT	10.0%		

PGU-2-F	4.0%	Clearing point [°C]:	80.5
CC-3-V1	10.0%	γ <sub>1</sub> [mPa·s, 20°C]:	67
CCP-V-1	14.0%	V <sub>10</sub> [V]:	1.80
CCG-V-F	10.0%		
CCP-20CF <sub>3</sub>	6.0%		
CCP-30CF <sub>3</sub>	6.0%		
CCP-40CF <sub>3</sub>	4.0%		
PCH-301	6.0%		
CC-4-V	18.0%		
PUQU-2-F	6.0%		
PUQU-3-F	8.0%		
PGP-2-3	8.0%		

# Example 12

PGU-2-F	6.0%	Clearing point [°C]:	80.0
PGU-3-F	2.0%	∆n [589 nm, 20°C]:	0.1048
CC-3-V1	11.0%	Δε [1 kHz, 20°C]:	5.7
CCP-V-1	12.0%	γ <sub>1</sub> [mPa·s, 20°C]:	69
CCG-V-F	10.0%	V <sub>10</sub> [V]:	1.68
CCP-30CF <sub>3</sub>	6.0%	V <sub>50</sub> [V]:	2.02
CCZU-3-F	12.0%	V <sub>90</sub> [V]:	2.48
PCH-301	7.0%	V <sub>90</sub> /V <sub>10</sub> :	1.478
CC-4-V	18.0%		
PUQU-2-F	4.0%		
PUQU-3-F	4.0%		
PGP-2-3	8.0%		

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CCZU-2-F	3.0%	Clearing point [°C]:	80.0
CCZU-3-F	14.0%	∆n [589 nm, 20°C]:	0.0934
PUQU-2-F	6.0%	Δε [1 kHz, 20°C]:	6.1
PUQU-3-F	8.0%	γ <sub>1</sub> [mPa·s, 20°C]:	69
CCG-V-F	9.0%	V <sub>10</sub> [V]:	1.67
CCP-V-1	12.0%	V <sub>50</sub> [V]:	2.01
CC-3-V1	13.0%	V <sub>90</sub> [V]:	2.52
CC-4-V	18.0%	V <sub>90</sub> /V <sub>10</sub> :	1.511
PCH-301	5.0%		
PGP-2-4	6.0%		
CVCP-2V-OT	6.0%		

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## Example 14

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PUQU-2-F	10.0%	Clearing point [°C]:	79.0
PUQU-3-F	10.0%	∆n [589 nm, 20°C]:	0.0943
CCP-V-1	16.0%	Δε [1 kHz, 20°C]:	5.6
CCP-V2-1	4.0%	γ <sub>1</sub> [mPa·s, 20°C]:	67
CCG-V-F	10.0%	V <sub>10</sub> [V]:	1.78
CC-3-V1	13.0%	V <sub>50</sub> [V]:	2.15
CC-4-V	18.0%	V <sub>90</sub> [V]:	2.71
PCH-301	6.0%	V <sub>90</sub> /V <sub>10</sub> :	1.522
PGP-2-4	2.0%		
CVCP-1V-OT	11.0%		***************************************

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#### Example 15

CCZU-3-F 6.0% 79.0 Clearing point [°C]: CCP-V-1 16.0% Δn [589 nm, 20°C]: 0.0940 CCG-V-F 10.0% Δε [1 kHz, 20°C]: 5.8 CC-4-V 18.0% 65  $\gamma_1$  [mPa·s, 20°C]: CC-3-V1 13.0% V<sub>10</sub> [V]: 1.71 V<sub>50</sub> [V]: PCH-301 2.06 6.0% PUQU-1-F 9.0% 2.59 V<sub>90</sub> [V]: PUQU-2-F 9.0%  $V_{90}/V_{10}$ : 1.519 PGP-2-4 3.0% CVCP-1V-OT 10.0%

Example 16

CCZU-3-F 12.0% Clearing point [°C]: 79.0 PUQU-2-F 8.0% ∆n [589 nm, 20°C]: 0.0938 PUQU-3-F 9.0% Δε [1 kHz, 20°C]: 5.8 CCP-V-1 12.0% γ<sub>1</sub> [mPa·s, 20°C]: 68 CC-3-V1 12.0%  $V_{10}[V]$ : 1.72 CC-4-V V<sub>50</sub> [V]: 18.0% 2.08 PCH-301 11.0%  $V_{90}[V]$ : 2.59 PGP-2-3 4.0%  $V_{90}/V_{10}$ : 1.506 CVCP-1V-OT 10.0% CCC-V-V 4.0%

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#### Example 17

CCZU-3-F 7.0% Clearing point [°C]: 80.0 CCP-V-1 16.0% ∆n [589 nm, 20°C]: 0.0936 CCG-V-F 10.0%  $\Delta \varepsilon$  [1 kHz, 20°C]: 5.9 CC-4-V 18.0% γ<sub>1</sub> [mPa·s, 20°C]: 67 CC-3-V1 13.0% 1.71 V<sub>10</sub> [V]: PCH-301 5.0% V<sub>50</sub> [V]: 2.07 V<sub>90</sub> [V]: PUQU-2-F 9.0% 2.60 PUQU-3-F  $V_{90}/V_{10}$ : 1.518 9.0% PGP-2-4 3.0% CVCP-1V-OT 10.0%

15 Example 18

CCZU-2-F 4.0% Clearing point [°C]: 0.08 CCZU-3-F 14.0% ∆n [589 nm, 20°C]: 0.0941 CCP-20CF3 4.0% Δε [1 kHz, 20°C]: 7.4 CCP-30CF3 3.0% γ<sub>1</sub> [mPa·s, 20°C]: 66 CCP-V-1 14.0%  $V_{10}[V]$ : 1.55 CCG-V-F 5.0% V<sub>50</sub> [V]: 1.87 PUQU-1-F 10.0% V<sub>90</sub> [V]: 2.33 PUQU-2-F 8.0%  $V_{90}/V_{10}$ : 1.505 PGP-2-4 5.0% CC-3-V1 13.0% CC-3-V 20.0%

79.0

Clearing point [°C]:

5.0%

## Example 19

PGU-1-F

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PGU-2-F	4.0%	Δn [589 nm, 20°C]:	0.1047
CC-3-V1	12.0%	Δε [1 kHz, 20°C]:	5.3
CCP-V-1	14.0%	γ <sub>1</sub> [mPa·s, 20°C]:	65
CCG-V-F	5.0%	V <sub>10</sub> [V]:	1.72
CCP-30CF3	6.0%	V <sub>50</sub> [V]:	2.07
CCZU-3-F	12.0%	V <sub>90</sub> [V]:	2.57
PCH-301	9.0%	V <sub>90</sub> /V <sub>10</sub> :	1.496
CC-4-V	18.0%		
PUQU-2-F	3.0%		
PUQU-3-F	4.0%		
PGP-2-4	8.0%		

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### Example 20

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CCZU-2-F	4.0%	Clearing point [°C]:	78.0
CCZU-3-F	14.0%	∆n [589 nm, 20°C]:	0.0992
PUQU-1-F	8.0%	Δε [1 kHz, 20°C]:	5.8
PUQU-2-F	6.0%	γ <sub>1</sub> [mPa·s, 20°C]:	66
CCP-V-1	13.0%	V <sub>10</sub> [V]:	1.67
CCG-V-F	7.0%	V <sub>50</sub> [V]:	2.00
CC-3-V1	15.0%	V <sub>90</sub> [V]:	2.47
CC-4-V	18.0%	V <sub>90</sub> /V <sub>10</sub> :	1.480
PCH-301	5.0%		
PGP-2-3	4.0%		
PGP-2-4	6.0%		

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#### Example 21

CCP-20CF3 4.0% Clearing point [°C]: 76.0 4.0% CCP-30CF3 Δε [1 kHz, 20°C]: 5.4 CCZU-3-F γ<sub>1</sub> [mPa·s, 20°C]: 58 4.0% PUQU-1-F 8.0% PUQU-2-F 8.0% CC-3-V1 6.0% CVCP-1V-OT 14.0% CVCP-2V-OT 4.0% PGP-2-4 8.0% CC-V-V1 40.0%

Comparative Example 1

CCP-2F.F.F	9.5%	Clearing point [°C]:	0.08
CCP-3F.F.F	1.5%	∆n [589 nm, 20°C]:	0.0773
CCZU-2-F	3.5%	Δε [1 kHz, 20°C]:	6.0
CCZU-3-F	9.0%	γ <sub>1</sub> [mPa·s, 20°C]:	81
CCP-20CF <sub>3</sub>	6.0%	V <sub>10</sub> [V]:	1.60
CCP-30CF <sub>3</sub>	4.0%	V <sub>50</sub> [V]:	1.97
CC-5-V	20.0%	V <sub>90</sub> [V]:	2.45
CC-3-V1	5.0%	V <sub>90</sub> /V <sub>10</sub> :	1.526
PCH-301	6.0%		
CGZP-2-OT	9.0%		
CCP-V-1	4.0%		
CCG-V-F	10.5%		
CGU-2-F	5.0%		
CCH-35	3.5%		
CCP-20CF <sub>3</sub> .F	3.5%		

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PGP-2-3	6.0%	Clearing point [°C]:	75.0
PGP-2-4	6.0%	∆n [589 nm, 20°C]:	0.1763
PGP-3-3	6.0%	Δε [1 kHz, 20°C]:	4.5
PCH-301	11.0%	γ <sub>1</sub> [mPa·s, 20°C]:	150
PCH-302	10.0%	V <sub>0</sub> [V]:	1.66
PGIGI-3-F	8.0%	$\gamma_1/(\Delta n)^2$ :	4826
GGP-2-F	10.0%	K <sub>1</sub> [pN]:	11.3
GGP-3-F	11.0%	K <sub>3</sub> [pN]:	14.4
GGP-5-F	10.0%	K <sub>3</sub> / K <sub>1</sub> :	1.27
CCP-V-1	8.0%		
CGG-3-F	14.0%		

15 Example 23

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PGP-2-3	6.0%	Clearing point [°C]:	77.0
PGP-2-4	8.0%	∆n [589 nm, 20°C]:	0.1695
PGP-3-3	6.0%	Δε [1 kHz, 20°C]:	4.4
PCH-301	15.0%	γ <sub>1</sub> [mPa·s, 20°C]:	156
PCH-302	14.0%	V <sub>0</sub> [V]:	1.73
GGP-2-F	9.0%	$\gamma_1/(\Delta n)^2$ :	5430
GGP-3-F	9.0%	K <sub>1</sub> [pN]:	11.7
GGP-5-F	9.0%	K <sub>3</sub> [pN]:	14.2
CGG-3-F	18.0%	K <sub>3</sub> / K <sub>1</sub> :	1.21
CBC-33F	3.0%		
CBC-53F	3.0%		

## Example 24

PGP-2-3	10.0%	Clearing point [°C]:	79.0
PGP-2-4	10.0%	∆n [589 nm, 20°C]:	0.1780
PGP-3-3	6.0%	Δε [1 kHz, 20°C]:	4.6
PCH-301	13.0%	γ <sub>1</sub> [mPa·s, 20°C]:	153
PCH-302	12.0%	V <sub>0</sub> [V]:	1.69
GGP-2-F	9.0%	$\gamma_1/(\Delta n)^2$ :	4829
GGP-3-F	10.0%	K <sub>1</sub> [pN]:	11.8
GGP-5-F	7.0%	K <sub>3</sub> [pN]:	14.0
CGG-3-F	19.0%	K <sub>3</sub> / K <sub>1</sub> :	1.19
CBC-33F	4.0%		

Example 25

PGP-2-3	11.0%	Clearing point [°C]:	80.5
PGP-2-4	11.0%	∆n [589 nm, 20°C]:	0.1813
PGP-3-2	6.0%	Δε [1 kHz, 20°C]:	4.6
PCH-301	12.0%	γ <sub>1</sub> [mPa·s, 20°C]:	157
PCH-302	11.0%	V <sub>0</sub> [V]:	1.69
GGP-2-F	9.0%	$\gamma_1/(\Delta n)^2$ :	4776
GGP-3-F	10.0%	K <sub>1</sub> [pN]:	11.9
GGP-5-F	7.0%	K <sub>3</sub> [pN]:	13.7
CGG-3-F	19.0%	K <sub>3</sub> / K <sub>1</sub> :	1.16
CBC-33F	4.0%		

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#### Example 26

PGP-2-3 12.0% 81.5 Clearing point [°C]: PGP-2-4 12.0% ∆n [589 nm, 20°C]: 0.1885 4.7 PGP-3-2 9.0% Δε [1 kHz, 20°C]: 157 PCH-301 11.0% γ<sub>1</sub> [mPa·s, 20°C]: PCH-302 9.0% V<sub>0</sub> [V]: 1.70  $\gamma_1/(\Delta n)^2$ : GGP-2-F 4419 9.0% GGP-3-F K<sub>1</sub> [pN]: 12.3 10.0% GGP-5-F 6.0% CGG-3-F 20.0% CBC-33F 2.0%

Example 27

PGP-2-3 13.0% Clearing point [°C]: 80.0 PGP-2-4 14.0% ∆n [589 nm, 20°C]: 0.1931 PGP-3-2 9.0% Δε [1 kHz, 20°C]: 4.8 PCH-301 12.0% γ<sub>1</sub> [mPa·s, 20°C]: 152 🔍 PCH-302 6.0% V<sub>0</sub> [V]: 1.66  $\gamma_1/(\Delta n)^2$ : GGP-2-F 9.0% 4076 GGP-3-F 11.0% K₁ [pN]: 12.3 GGP-5-F 6.0% K<sub>3</sub> [pN]: 12.7  $K_3 / K_1$ : CGG-3-F 20.0% 1.04

PGP-2-3 14.0% Clearing point [°C]: 80.5 ∆n [589 nm, 20°C]: PGP-2-4 15.0% 0.1939 PGP-3-2 9.0% Δε [1 kHz, 20°C]: 4.8 PCH-301 <sub>γ1</sub> [mPa⋅s, 20°C]: 157 17.0% GGP-2-F  $V_0$  [V]: 1.66 9.0% GGP-3-F  $\gamma_1/(\Delta n)^2$ : 10.0% **4**176 GGP-5-F 6.0% K<sub>1</sub> [pN]: 11.8 CGG-3-F K<sub>3</sub> [pN]: 20.0% 12.5  $K_3/K_1$ : 1.06

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#### Example 29

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PGP-2-3	15.0%	Clooring point (°C1)	04 5
		Clearing point [°C]:	84.5
PGP-2-4	15.0%	Δn [589 nm, 20°C]:	0.2001
PGP-3-2	9.0%	Δε [1 kHz, 20°C]:	5.3
PCH-301	13.0%	γ₁ [mPa⋅s, 20°C]:	172
GGP-2-F	10.0%	V <sub>0</sub> [V]:	1.64
GGP-3-F	10.0%	$\gamma_1/(\Delta n)^2$ :	4296
GGP-5-F	7.0%	K <sub>1</sub> [pN]:	12.4
CGG-3-F	21.0%	K <sub>3</sub> [pN]:	12.2
		K <sub>3</sub> / K <sub>1</sub> :	0.98

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# Example 30

PGP-2-3	15.0%	Clearing point [°C]:	83.0
PGP-2-4	15.0%	∆n [589 nm, 20°C]:	0.2015
PGP-3-2	9.0%	Δε [1 kHz, 20°C]:	5.0
PCH-301	12.0%	γ <sub>1</sub> [mPa·s, 20°C]:	159
GGP-2-F	9.0%	V <sub>0</sub> [V]:	1.72
GGP-3-F	10.0%	$\gamma_1/(\Delta n)^2$ :	3916
GGP-5-F	6.0%	K <sub>1</sub> [pN]:	13.1
CGG-3-F	20.0%	K <sub>3</sub> [pN]:	13.0
PP-1-2V1	4.0%	K <sub>3</sub> / K <sub>1</sub> :	0.99

Example 31

PGP-2-3	16.0%	Clearing point [°C]:	87.5
PGP-2-4	16.0%	∆n [589 nm, 20°C]:	0.2113
PGP-3-2	11.0%	Δε [1 kHz, 20°C]:	4.8
PCH-301	9.0%	y <sub>1</sub> [mPa·s, 20°C]:	174
GGP-2-F	9.0%	V <sub>0</sub> [V]:	1.83
GGP-3-F	10.0%	$\gamma_1/(\Delta n)^2$ :	3897
GGP-5-F	6.0%	K <sub>1</sub> [pN]:	14.5
CGG-3-F	18.0%	K <sub>3</sub> [pN]:	13.6
PP-1-2V1	5.0%	K <sub>3</sub> / K <sub>1</sub> :	0.94

## Comparative Example 2

FET-2CI	15.0%	Clearing point [°C]:	80.3
FET-3CI	6.0%	∆n [589 nm, 20°C]:	0.2106
FET-5CI	19.0%	Δε [1 kHz, 20°C]:	5.5
PGIGI-3-CI	10.0%	γ <sub>1</sub> [mPa·s, 20°C]:	299
PGIGI-5-CI	13.0%	V <sub>0</sub> [V]:	1.76
PCH-301	10.0%	$\gamma_1/(\Delta n)^2$ :	6741
GGP-5-CI	16.0%	K <sub>1</sub> [pN]:	14.4
BCH-3F.F	11.0%	K <sub>3</sub> [pN]:	19.6
		K <sub>3</sub> / K <sub>1</sub> :	1.36

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#### **Patent Claims**

1. Liquid-crystalline medium based on a mixture of polar compounds of positive or negative dielectric anisotropy, characterised in that it comprises one or more compounds of the general formula I

 $R^1$  O O  $R^2$ 

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R<sup>1</sup> and R<sup>2</sup> each, independently of one another, identically or differently, denote H, an alkyl radical having 1 to 12 C atoms which is unsubstituted, monosubstituted by CN or CF<sub>3</sub> or at least monosubstituted by halogen, where, in addition, one or more CH<sub>2</sub> groups in these radicals may each, independently of one another, be replaced by -O-, -S-, -CH=CH-, -C≡C-, -CO-, -CO-O-, -O-CO- or -O-CO-O- in such a way that O atoms are not linked directly to one another.

- 2. Medium according to Claim 1, characterised in that, in the compound of the formula I, R<sup>1</sup> and/or R<sup>2</sup>, independently of one another, identically or differently, denote H, a straight-chain alkyl radical having 1 to 9 C atoms or a straight-chain alkenyl radical having 2 to 9 C atoms.
- 3. Medium according to Claim 1 or 2, characterised in that it comprises one or more compounds selected from the group of the compounds of the sub-formulae la to ld:

$$alkyl^{1} \qquad O \qquad O \qquad alkyl^{2}$$

$$alkyl^{1} \qquad O \qquad O \qquad O \qquad alkenyl^{2}$$

where the term "alkyl<sup>1</sup>" and "alkyl<sup>2</sup>" in each case, independently of one another, identically or differently, denotes a hydrogen atom or an alkyl radical having 1 to 9 C atoms, preferably a straight-chain alkyl radical having 1 to 5 C atoms, and the term "alkenyl<sup>1</sup>" and "alkenyl<sup>2</sup>" in each case, independently of one another, identically or differently, denotes an alkenyl radical having 2 to 9 C atoms, preferably a straight-chain alkenyl radical having 2 to 5 C atoms.

4. Medium according to at least one of the preceding claims, characterised in that it comprises one or more compounds selected from the group of the compounds of the sub-formulae I1 to I25:

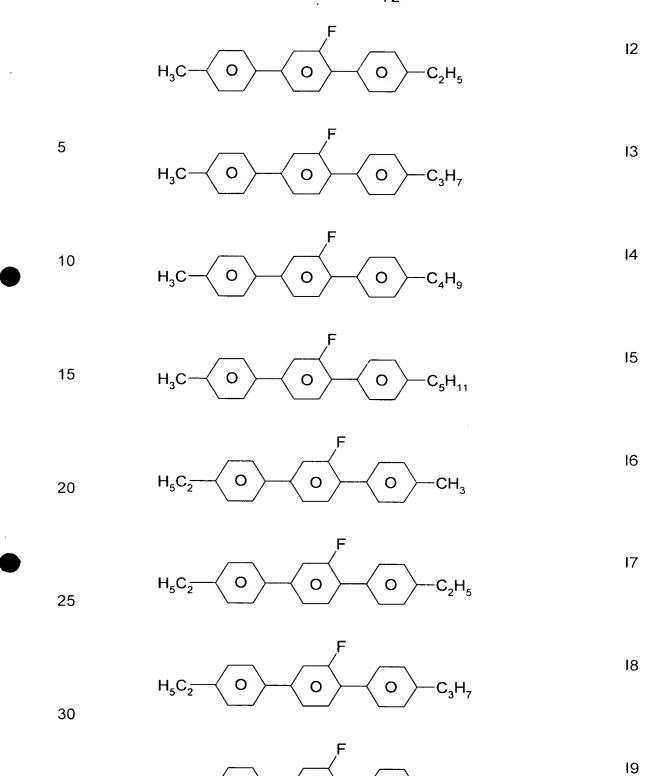
$$H_3C \longrightarrow O \longrightarrow O \longrightarrow CH_3$$

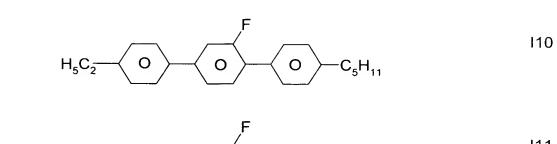
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$$H_7C_3$$
  $O$   $O$   $CH_3$ 

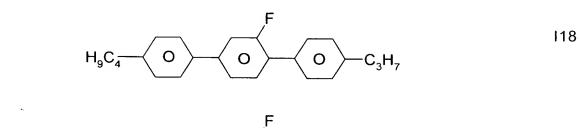
$$H_7C_3 \longrightarrow O \longrightarrow O \longrightarrow C_3H_7$$

$$H_7C_3 \longrightarrow O \longrightarrow O \longrightarrow C_4H_9$$

$$H_7C_3$$
  $O$   $O$   $O$   $C_5H_{11}$ 

$$H_9C_4$$
 O  $O$   $O$   $CH_3$ 

$$H_9C_4$$
  $O$   $O$   $O$   $C_2H_5$ 



$$H_{9}C_{4} \longrightarrow O \longrightarrow O \longrightarrow C_{4}H_{9}$$

$$H_9C_4$$
  $O$   $O$   $O$   $C_5H_{11}$ 

$$H_{11}C_{5} \longrightarrow O \longrightarrow CH_{3}$$

$$H_{11}C_{5} \longrightarrow O \longrightarrow O \longrightarrow C_{2}H_{5}$$

$$H_{11}C_5 \longrightarrow O \longrightarrow O \longrightarrow C_3H_7$$

$$H_{11}C_5$$
  $O$   $O$   $O$   $C_4H_9$ 

$$H_{11}C_5$$
  $O$   $O$   $O$   $C_5H_{11}$ 

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5. Medium according to at least one of the preceding claims, characterised in that the proportion of compounds of the formula I in the mixture as a whole is 1 to 60% by weight.

6. Medium according to at least one of the preceding claims, characterised in that it additionally comprises one or more compounds selected from the group consisting of compounds of the general formulae II to X:

$$R^0 \xrightarrow{H} H \xrightarrow{O} X^0$$

$$R^0 \longrightarrow H \longrightarrow Z^0 \longrightarrow H \longrightarrow Q^1$$

$$R^0$$
  $H$   $Z^0$   $O$   $X^0$   $V$ 

$$R^0 \xrightarrow{H} O \xrightarrow{Y^3} O \xrightarrow{Y^1} V$$

$$R^0 \longrightarrow L^0 \longrightarrow L^0$$

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$$R^{0} \xrightarrow{H} C \xrightarrow{Y^{3}} Z^{0} \xrightarrow{Q^{1}} X^{0}$$

$$VII$$

$$R^0 \xrightarrow{Q^5} Q \xrightarrow{Q^4} Q \xrightarrow{Q^2} X^0 \qquad \qquad \forall III$$

$$R^{0} \xrightarrow{Q^{5}} Z^{0} \xrightarrow{Q^{4}} Q \xrightarrow{Q^{2}} X^{0}$$

$$IX$$

$$R^0 \longrightarrow O \longrightarrow Z^0 \longrightarrow Z^0 \longrightarrow X^0 \qquad \qquad \chi$$

in which the individual radicals have the following meanings:

R<sup>0</sup>: n-alkyl, oxaalkyl, fluoroalkyl or alkenyl, each having up to 9 C atoms;

X<sup>0</sup>: F, CI, halogenated alkyl or halogenated alkoxy having 1 to 6 C atoms, or halogenated alkenyl having 2 to 6 C atoms;

$$Z^0$$
:  $-CF_2O_-$ ,  $-OCF_2-$ ,  $-CH_2O_-$ ,  $-OCH_2-$ ,  $-COO_-$ ,  $-O-CO_-$ ,  $-CH=CH_-$ ,  $-C_2H_4-$ ,  $-C_2F_4-$ ,  $-CH_2CF_2-$ ,  $-CF_2CH_2-$  or  $-C_4H_8-$ ;

 $Y^1$ ,  $Y^2$ ,  $Y^3$ ,  $Y^4$ ,  $Y^5$  and  $Y^6$ : each, independently of one another, H or F;

r: 0 or 1.

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7. Medium according to Claim 6, characterised in that the proportion of compounds of the formulae II to X in the mixture as a whole is 20 to 70% by weight.

8. Medium according to at least one of the preceding claims, characterised in that it comprises one or more compounds selected from the group consisting of compounds of the general formulae XI to XVII:

$$R^1 - \left( \begin{array}{c} H \\ \end{array} \right) - Z^1 - \left( \begin{array}{c} H \\ \end{array} \right) - R^2$$

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$$R^1 \longrightarrow Z^1 \longrightarrow Q$$
  $Q \longrightarrow R^2$ 

$$R^{1} \longrightarrow Q \longrightarrow Z^{1} \longrightarrow Q \longrightarrow R^{2}$$
 XIII

$$R^1 \longrightarrow R^2$$
 XIV

$$R^1 \longrightarrow R^2 \longrightarrow R^2$$
 XV

$$R^1 \longrightarrow R^2 \longrightarrow Z^1 \longrightarrow Q \longrightarrow R^2$$
 XVI

$$R^1 - O - Z^1 - O - Z^2 - R^2$$

in which the individual radicals have the following meanings:

R<sup>1</sup> and R<sup>2</sup>: independently of one another, identically or differently, n-alkyl, n-alkoxy or alkenyl, each having up to 9 C atoms; and

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 $Z^1$  and  $Z^2$ : independently of one another, identically or differently, a single bond, -CF<sub>2</sub>O-, -OCF<sub>2</sub>-, -CH<sub>2</sub>O-, -OCH<sub>2</sub>-, -COO-, -O-CO-, -CH=CH-, -C<sub>2</sub>H<sub>4</sub>-, -C<sub>2</sub>F<sub>4</sub>-, -CH<sub>2</sub>CF<sub>2</sub>-, -CF<sub>2</sub>CH<sub>2</sub>or -C<sub>4</sub>H<sub>8</sub>-.

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9. Medium according to Claim 8, characterised in that the proportion of compounds of the formulae XI to XVII in the mixture as a whole is 5 to 70% by weight.

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Use of a liquid-crystalline medium according to at least one of the 10. preceding claims for electro-optical purposes.

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Electro-optical display devices containing a liquid-crystalline medium according to at least one of Claims 1 to 9.

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#### **Abstract**

The present invention relates to a liquid-crystalline medium based on a mixture of polar compounds of positive or negative dielectric anisotropy which is characterised in that it comprises one or more compounds of the general formula I

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$$R^1$$
  $O$   $O$   $R^2$ 

in which

each, independently of one another, identically or differently, denote H, an alkyl radical having 1 to 12 C atoms which is unsubstituted, monosubstituted by CN or CF<sub>3</sub> or at least monosubstituted by halogen, where, in addition, one or more CH<sub>2</sub> groups in these radicals may each, independently of one another, be replaced by -O-, -S-, -CH=CH-, -C=C-,

-CO-, -CO-O-, -O-CO- or -O-CO-O- in such a way that O atoms are not linked directly to one another,

to the use thereof for electro-optical purposes, and to electro-optical display devices which contain this medium.